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Feature Article

Multigraft copolymer superelastomers: Synthesis morphology, and properties

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Dedicated to Professor Nikos Hadjichristidis in recognition of his contribution to polymer science.

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ABSTRACT

The synthesis of well-defined multigraft copolymers having a polydiene backbone with polystyrene side chains is briefly reviewed, with particular focus on controlling branch point spacing and branch point functionality. Use of living anionic polymerization and chlorosilane linking chemistry has led to the synthesis of series of materials having regularly spaced trifunctional (comb), tetrafunctional (centipede), and hexafunctional (barbwire) branch points. The morphologies of these materials were characterized by transmission electron microscopy and small-angle X-ray scattering, and it was found that the morphologies were controlled by the local architectural asymmetry associated with each branch point. Mechanical properties studies revealed that such multigraft copolymers represent a new class of thermoplastic elastomers (TPEs) with superior elongation at break and low residual strains as compared to conventional TPEs.

1. Introduction

Thermoplastic elastomers (TPEs) represent an important segment of the worldwide elastomer market due to their combination of mechanical properties comparable to vulcanized rubbers and straightforward processing similar to that of thermoplastics [1]. TPEs are also of interest because of their capacity to self-assemble to form ordered phase separated structures having nanoscale dimensions, with morphologies and properties tunable by controlling the volume fractions of hard and soft segments [2]. Two of the most important commercial classes of TPEs commercially, as well as the most studied class of TPEs in terms of their fundamental properties, are SIS and SBS triblock copolymers. Here S represents glassy polystyrene (PS) end-blocks and I and B represent rubbery polyisoprene (PI) and polybutadiene (PBD) mid-blocks, respectively. For these materials the morphology formed, and thus the mechanical properties, are directly linked to the volume fractions of the two components.

The use of branching to improve the properties of styrene/diene TPEs has been explored since the 1970s. Fetters and coworkers synthesized star-block copolymers, star polymers where each arm is a block copolymer, having PS outer blocks and PI inner blocks and reported improved tensile strength relative to linear triblocks of comparable composition and segment molecular weights [3]. Commercial star-block copolymers based on S/I and S/B compositions have been commercialized by companies such as Phillips, BASF, etc. Graft copolymers are another class of branched block copolymers having a backbone composed of one type of polymer with pendant side chains that are chemically different from the backbone [4]. The concept of using multigraft copolymers as TPEs is interesting, because if the backbone is chosen as the soft segment with hard segments as

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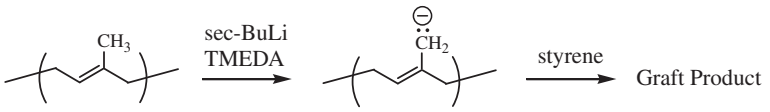


Fig. 1. Synthesis of graft copolymer by metallation of polyisoprene.

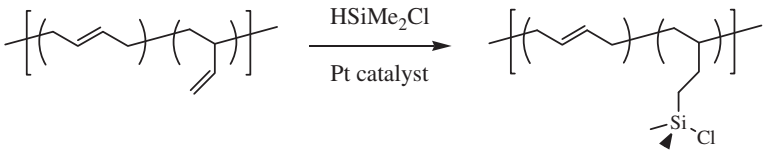


Fig. 2. Hydrosilylation of polybutadiene.

the side chains there will be multiple tether points connecting the rubbery backbone to reinforcing rigid domain. This would appear to offer potential to create elastomers exhibiting improved mechanical properties.

2. Synthesis of multigraft copolymer TPEs

The first work on synthesis of multigraft copolymers by metallation of a polydiene backbone (a "grafting from strategy") dates back to the late 1960s [5–7]. These works were plagued by serious degradation of the polydiene backbones. The first systematic study of graft copolymers having polydiene backbones with PS grafts as TPEs was work of Falk and coworkers [8]. These workers employed milder metallation conditions in order to minimize polymer degradation. They concluded that the elastomeric properties of their PBD-g-PS multigraft copolymers were similar to that of corresponding SBS triblock copolymers and offer the advantage of higher melt flow [8].

Hadjichristidis and Roovers [9] synthesized PI-g-PS multigraft copolymers (see Fig. 1) by following the synthetic approach of Falk et al. but improved the level of control during the synthesis by employing high vacuum line techniques [10,11] in a vessel equipped with an optical cell.

Even under these optimized conditions, some homopolystyrene is present and must be removed by fractionation. Isolation of the PS is in fact useful in characterizing the molecular architecture of the resulting copolymers. The branch points are randomly spaced along the PI backbone and the branch points are trifunctional (one side chain per branching site).

Cameron and Qureshi employed a "grafting to" approach to make PI-g-PS multigraft copolymers having randomly placed trifunctional branch points [12]. This involved the use of hydrosilation chemistry to introduce chlorosilane functionality onto 1,2-units of PBD, followed by reaction with poly(styryllithium) (Fig. 2). The grafting to approach offers the advantage of being able to characterize both the backbone and side chains prior to the grafting reaction and the reaction of the PS anions with chlorosilane groups is known to be free of side reactions.

Xenidou and Hadjichristidis subsequently extended this strategy to make PBD-g-PS multigrafts carrying two PS

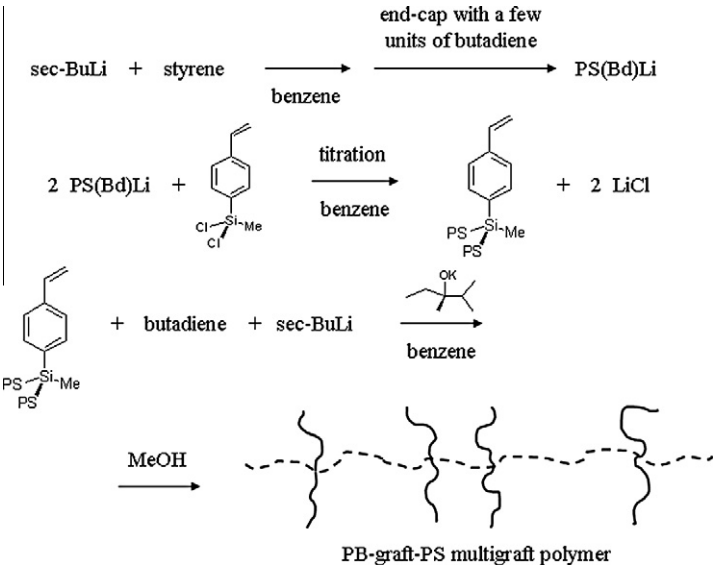


Fig. 3. Synthesis of polybutadiene graft copolymer by *in situ* macromonomer preparation.

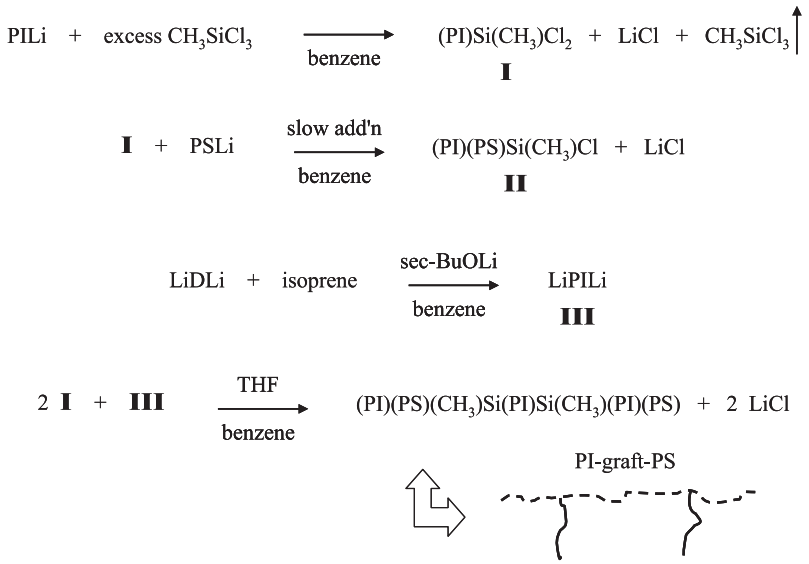


Fig. 4. Synthesis of poly(isoprene-graft-styrene) "π" copolymer by modular strategy.

grafts per randomly placed branch point (i.e. tetrafunctional branch points) by employing dichloromethylsilane in the hydrosilylation step [13].

In situ synthesis and polymerization of macromonomers has been shown to be an effective strategy for synthesis of comb and graft polymers [14]. This same macromonomer approach using copolymerization of PS-based macromonomers with diene monomers in the presence of randomizers has been used to make multigraft copolymers having polydiene backbones with randomly placed tetrafunctional and pentafunctional multigrafts [15,16]. The synthesis of PBD-g-PS "doubly tailed" multigrafts is shown in Fig. 3.

Beginning in 1990, Mays and Hadjichristidis initiated systematic programs on synthesis of PI-g-PS (and to a lesser extent PBD-g-PS) graft copolymers, starting with species having a single branch point, which could be located in the middle of the PI backbone or moved off-center to a desired location along the PI backbone, and then to more complex structures including regular doubly grafted structures such as π and H shaped graft copolymers [17]. Their syntheses involved the use of well-established chlorosilane linking chemistry [18] to connect together individual segments of the graft copolymer that bear anions at one chain end or at both ends, as demonstrated in Fig. 4 for the synthesis of π shaped graft copolymers.

This work allowed precise control over the number of branch points and branch point spacing, as well as backbone and side chain lengths.

The application of this chemistry to synthesize multigraft copolymers having regularly spaced branch points and control of the number of branches per branch point was first demonstrated by Hadjichristidis and Mays [19] and extended by Uhrig and Mays [20]. As shown in Fig. 5, the strategy exploits a step growth reaction between two

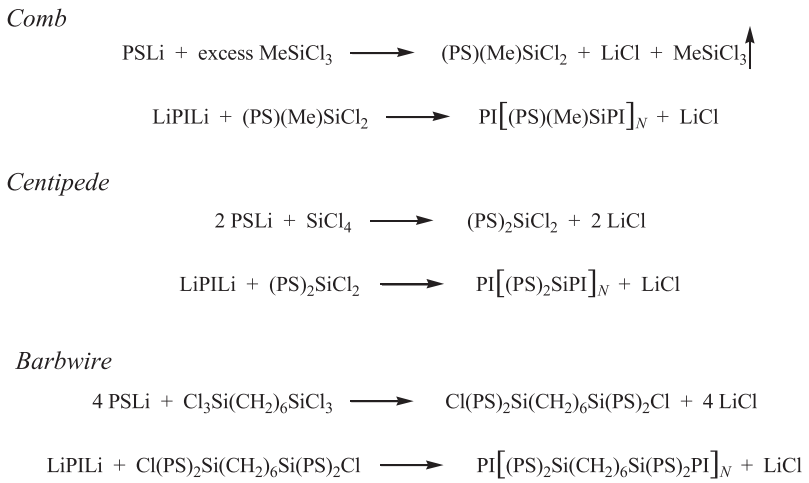


Fig. 5. Synthesis of poly(isoprene-graft-styrene) multigraft copolymers by modular strategy.

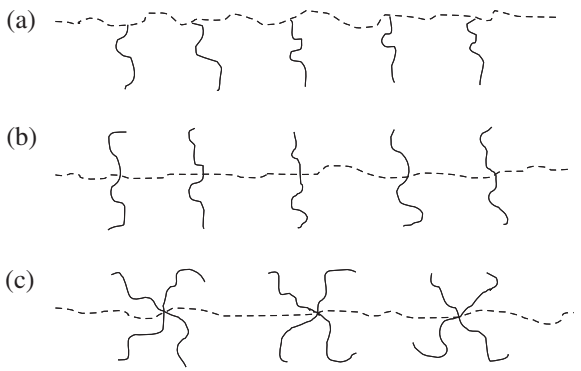


Fig. 6. Multigraft copolymer architectures: (a) trifunctional branch points, "comb"; (b) tetrafunctional branch points,"centipede"; (c) hexafunctional branch points, "barbwire".

polymeric macromonomers: one being a PS bearing two reactive chlorosilane groups and the other being a PI having reactive anions at both ends of the chain.

These materials, having trifunctional, tetrafunctional, and hexafunctional branch points are called, respectively, "comb", "centipede", and "barbwire" architectures [19,20] and are illustrated in Fig. 6.

While both the PI backbone segments and the PS branches of these materials have very narrow polydispersity indices (PDI) since they are made by living anionic polymerization, due to the step-growth polymerization mechanism that is used to build the multigraft structures the final products have PDIs of 2 or slightly higher. However, this polydispersity reflects primarily the presence of structures having different numbers of branch points and by solvent/nonsolvent fractionation several specimens having narrow PDI and different average numbers of branches may be isolated [19,20]. Such specimens are ideal for studying the influence of branching architecture and degree of branching on properties of multigraft copolymers.

3. Morphology of multigraft copolymers

Milner developed a self-consistent mean field model that predicts the influence of architectural and conformational asymmetry on block copolymer morphology in the strong segregation limit [21]. Milner introduced an asymmetry parameter ε, defined as $\varepsilon = (n_A/n_B)\ (l_A/l_B)^{1/2}$ where n_A and n_B are the numbers of chemically different chains connected together in the star and l_A and l_B reflect differences in conformational flexibility of the two polymeric species. This theory predicts to a good approximation the morphology of miktoarm stars of various architectures as a function of Φ_B, the volume fraction of the B component.

In order to apply Milner's theory to graft copolymer architectures having more than one branch point the "constituting miktoarm star" concept, illustrated in Fig. 7, may be used [22].

The idea is basically that it is the local symmetry or asymmetry in the multigraft that controls morphology. For example, a centipede multigraft copolymer may be considered as a number of A_2B_2 miktoarm stars that are linked together. In Fig. 8, morphologies observed for four centipede copolymers are plotted on Milner's miktoarm star phase diagram; the values in the boxes are the PS volume fractions.

All but the "67" sample exhibit the morphology predicted by Milner. This specimen is expected, based on the Milner model, to exhibit a bicontinuous morphology but instead forms a cylindrical morphology. When specimens made from the same backbone and side chain segments but having different numbers of branch points were investigated it was found that they exhibit the same morphologies, as expected, but the extent of long range order

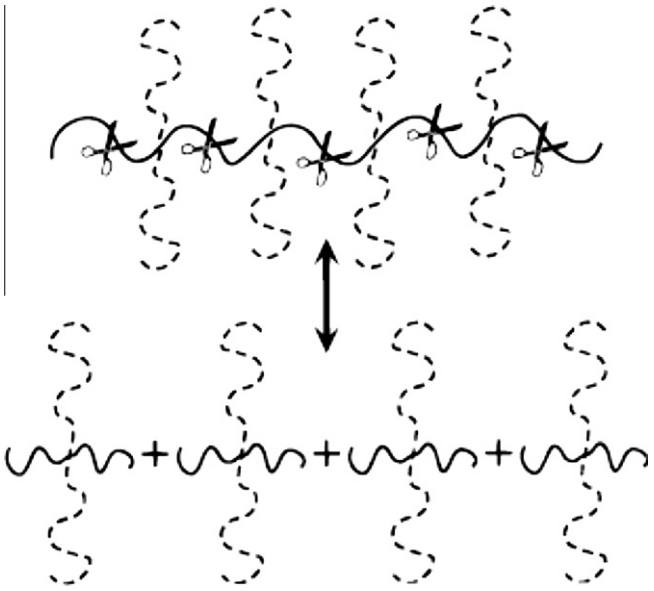


Fig. 7. A multigraft is understood by its "constituting block copolymer" repeat unit.

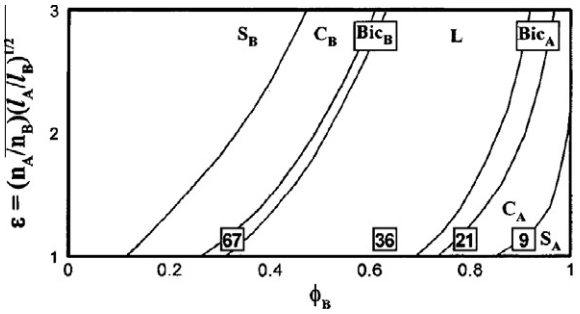


Fig. 8. Mapping of experimentally observed centipede morphological behavior onto Milner's theoretical predictive diagram.

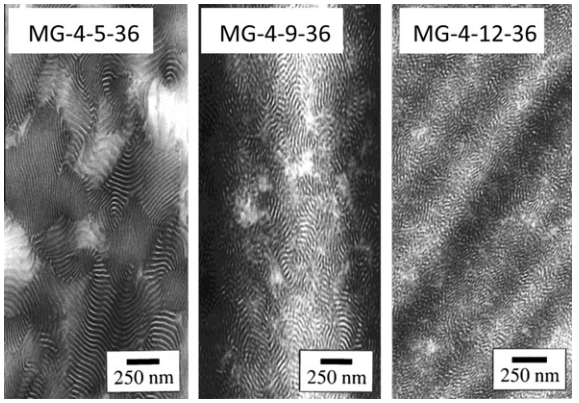


Fig. 9. TEM micrographs of centipedes with 36% polystyrene content.

decreased as the number of branch points was increased [22]. This is seen in Fig. 9 where "MG" represents multigraft, the "4" indicates tetrafunctional branch points or centipede architecture, "5", "9", and "12" represent the number of branch points, and "36" represents the volume percent PS in the materials.

4. Mechanical properties of multigraft copolymers

Multigraft copolymers show high strains at break and, in comparison to commercial materials like Kraton (20% PS) and Styroflex (58% PS), they retain adequate tensile strengths. This was demonstrated by Weidisch and coworkers by mechanical testing of regularly spaced tetrafunctional multigraft copolymers exhibiting unorientated morphologies [23]. For a multigraft copolymer with 22% PS and 10 branch points the strain at break is almost twice that observed for Kraton with 20% PS. The high tensile strength is attributed to a sufficient molecular weight of the PS grafts. In hysteresis tests multigraft copolymers show low residual strains when stretched previously to elongations above 1000% (Fig. 10). Model fits according to the non-affine tube model and an energy-based softening model were performed in other works [27]. In particular for multigraft copolymers with spherical morphologies, low softening characteristics, low residual strains and large extensibilities were found, and evidence could be given by the softening parameter b and the average number of statistical segments between two successively trapped entanglements (Fig. 11).

Functionality and number of branch points have a strong effect on tensile strength. It was found that σ_B increases approximately linearly with either parameter within the investigated region (Fig. 12). It is possible to correlate the increase in number of branch points with decrease in grain size and long range order, finer distribution of the PS microdomains, and resultant augmentation of mechanical properties. For TPEs in general, the PS domains act as 'chemical', yet resolvable crosslinks, similar to crosslinked rubber.

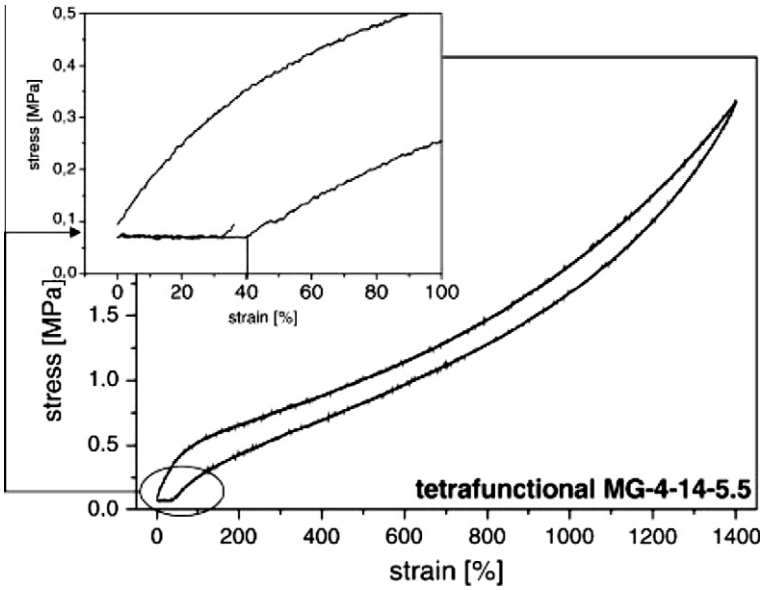


Fig. 10. Hysteresis curve of a tetrafunctional multigraft copolymer with 14 vol-% PS and 5.5 branch points.

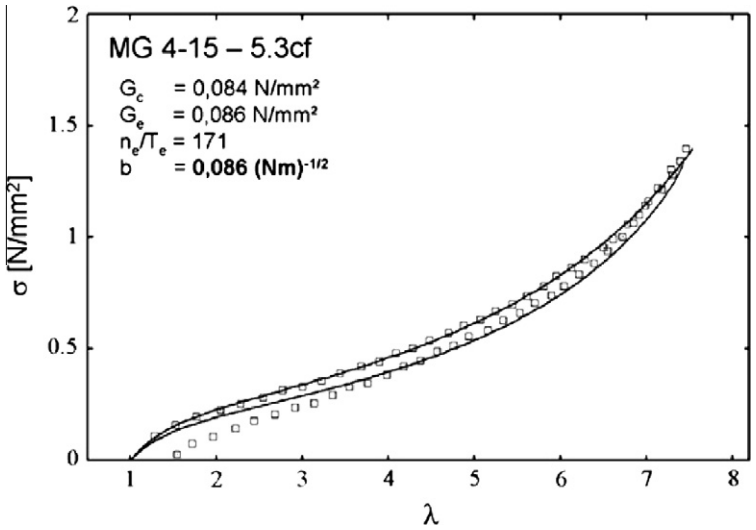


Fig. 11. Hysteresis data with model fits according to the non-affine tube model and the softening model for a tetrafunctional multigraft copolymer with 15 vol-% PS and 5.3 branch points (coarsely fractionated, second hysteresis cycle) [24,27].

In contrast to SBS triblocks and trifunctional graft copolymers, multigrafts with tetrafunctional branch points provide improved stress transfer between the polymer matrix and the PS domains. This was demonstrated additionally by computer simulations of the molecular interactions between PS grafts in the nanodomains [25]. The studies on hysteresis behavior revealed that physical crosslinking strongly influences hysteresis characteristics at high deformations. Evidence was given further by the dynamic flocculation model, which assumes successive break-down and re-agglomeration of filler clusters [26]. From the fit parameters of the model it was suggested that the deformation mechanism of multigraft copolymers is comparable to that of filled elastomers [26]. The stress softening was shown to be in correlation to the number of branch points and it can be reduced by improved distribution of the PS domains.

Results from relaxation tests and application of rubber elasticity model to stress strain data revealed that (i) the PS domains of high continuity result in lower stress relaxation, and (ii) a highly ramified PS domain structure lowers the physical cross-link modulus during the first hysteresis cycle (Fig. 13). The latter was attributed to a preferred break down of PS-PS domain bridges due to local stress concentrations [28]. In these works the PS-domains of the multigrafts were considered as filler

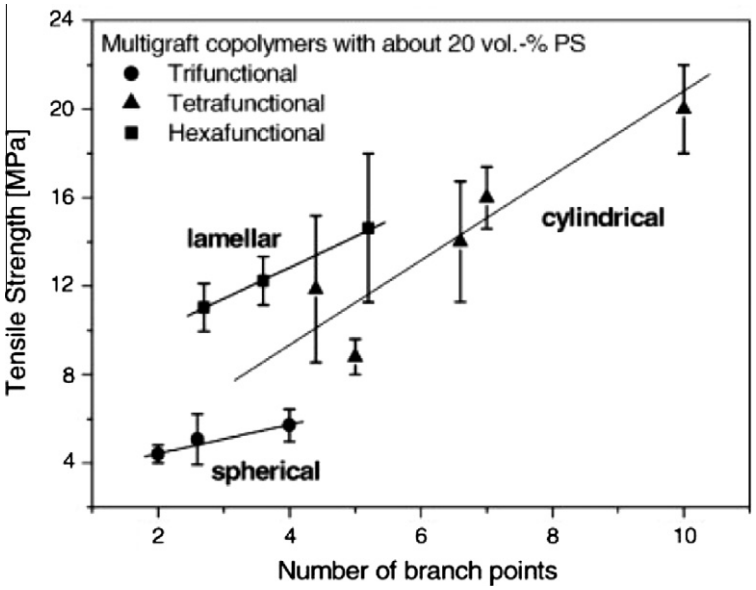


Fig. 12. Influence of the number of branch points on tensile strength, s_B [24,28].

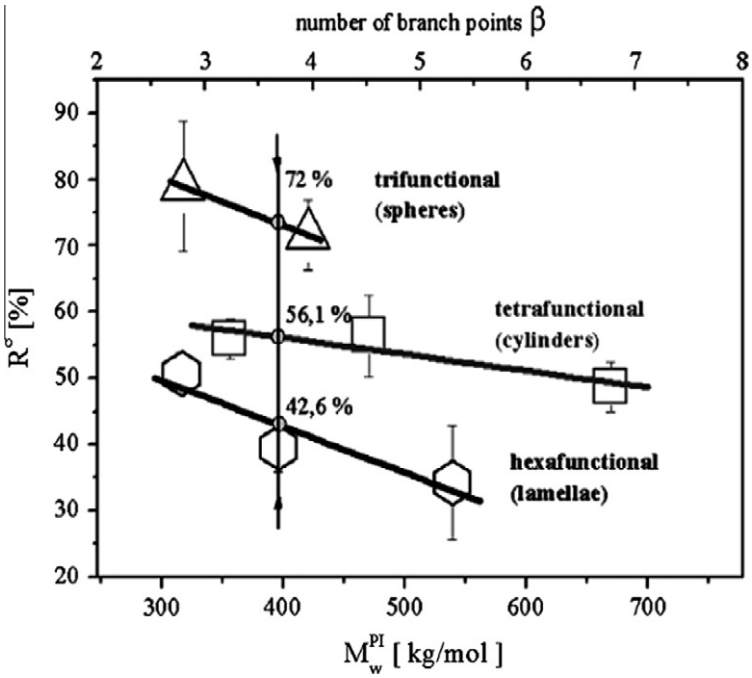


Fig. 13. Influence of the number of branch points on stress relaxation, R^s.

particles assuming a spherical shape, and it is relevant to consider their true shape especially during the deformation process.

Detailed information on microstructural damage and deformation mechanisms were obtained by synchrotron small-angle X-ray scattering (SAXS) and *in situ* deformation Fourier transform infrared spectroscopy (FTIR) characterization [29]. It was suggested that on the molecular level, PS domains can be termed double functionalized (the number of PI chains connected to one PS-domain is for graft copolymers usually twice as compared to triblock copolymers) and this may dramatically improve the stress transformation between the two phases [29]. Further, by *in situ* deformation FTIR molecular orientation was found to be similar for PI and PS, suggesting a large interface between PI and PS – phase and therefore to mainly soft physical cross-links, represented by the PS domains.

5. Conclusions

Well-defined graft copolymers having multiple regularly spaced branch points of controlled functionality may be synthesized by anionic polymerization and chlorosilane linking chemistry. The structure-morphology relationships for these materials may be understood by applying Milner's model to the miktoarm star that constitutes the repeating unit of the multigraft copolymer. Multigraft copolymers exhibit superelastomeric properties: strain at break can far exceed that of conventional triblock copolymer TPEs with low residual strains. This behavior is attributed to improved stress transfer between the phases and multiple tethering of the elastomeric backbone to the glassy domains.

Acknowledgments

We dedicate this paper to our friend and long-time collaborator, Professor Nikos Hadjichristidis, on the occasion of his retirement. Some of Professor Hadjichristidis' many seminal contributions to synthesis and understanding of multigraft copolymer TPEs are documented in this paper. DU and JM acknowledge support by the Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy. JM also acknowledges support from the Division of Materials Science and Engineering, Office of Basic Energy Sciences, US Department of Energy, under contract number DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC. RS and RW acknowledge financial support of the German Science Foundation (DFG).

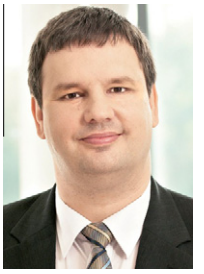
References

[1] Legge NR, Holden G, Schroeder HE, editors. Thermoplastic elastomers. Munich: Hanser; 1987. p. 1–4.
[2] Rader CP. In: Kaplan WL, editor. Modern plastics encyclopedia, vol. 72. New York: McGraw-Hill; 1996.
[3] Bi LK, Fetters LJ. Synthesis and properties of block copolymers. 3. Polystyrene-polydiene star block copolymers. Macromolecules 1976;9:732–42.
[4] Mays JW, Gido SP. McGraw-Hill yearbook of science and technology. New York: McGraw-Hill; 2003. p. 163.
[5] Harada H, Shiina K, Minoura Y. Lithiation of diene polymers. J Polym Sci Part A-1 1968;6:559–73.
[6] Minoura Y, Harada H. Anionic graft copolymerization of diene polymers with vinyl monomers. J Polym Sci Part A-1 1969;7:3–14.
[7] Tate DP, Halasa AF, Webb FJ, Koch RW, Oberster AE. "Metallation of unsaturated polymers and formation of graft copolymers". J Polym Sci Part A-1 1971;9(9):139–45.
[8] Falk JC, Schlott RJ, Hoeg DF, Pendleton JF. New thermoplastic elastomers. Styrene grafts on lithiated polydienes and their hydrogenated counterparts. Rubber Chem Technol 1973;46:1044–54.

[9] Hadjichristidis N, Roovers J. Conformation of poly(isoprene-gstyrene) in dilute solution. J Polym Sci Polym Phys Ed 1978;16:851–8.
[10] Hadjichristidis N, Iatrou H, Pispas S, Pitsikalis M. Anionic polymerization: high vacuum techniques. J Polym Sci Part A: Polym Chem 2000;38:3211–34.
[11] Uhrig D, Mays JW. Experimental techniques in high-vacuum anionic polymerization. J Polym Sci Part A: Polym Chem 2005;43:6179–222.
[12] Cameron GC, Qureshi MY. "Grafting of polybutadiene functionalised with chlorosilane groups". Macromol Chem Rapid Commun 1981;2:287–91.
[13] Xenidou M, Hadjichristidis N. Synthesis of model multigraft copolymers of butadiene with randomly placed single and double polystyrene branches. Macromolecules 1998;31:5690–4.
[14] Knauss DM, Al-Muallem AH, Huang T, Wu DT. Polystyrene with dendritic branching by convergent living anionic polymerization. Macromolecules 2000;33:3557–68;
Al-Muallem HA, Knauss DM. Graft copolymers from star-shaped and hyperbranched polystyrene macromonomers. J Polym Sci Polym Chem Ed 2001;39:3547–55;
Pantazis D, Chalari I, Hadjichristidis N. Anionic polymerization of styrenic macromonomers. Macromolecules 2003;36:3783–5.
[15] Driva P, Iatrou H, Lohse DJ, Hadjichristidis N. Anionic homo- and copolymerization of double-tailed macromonomers: a route to novel macromolecular architectures. J Polym Sci Part A: Polym Chem 2005;43:4070–8.
[16] Nikopoulou A, Iatrou H, Lohse DJ, Hadjichristidis N. Anionic homo- and copolymerization of styrenic triple-tailed polybutadiene macromonomers. J Polym Sci Part A: Polym Chem 2007;45:3513–23.
[17] Mays JW. Synthesis of "simple graft" poly(isoprene-g-styrene) by anionic polymerization. Polymer Bulletin 1990;23:247–50;
Hadjichristidis N, Iatrou H, Behal SK, Chludzinski JJ, Disko MM, Garner RT, et al. Morphology and miscibility of miktoarm styrene-diene copolymers and terpolymers. Macromolecules 1993;26:5812–5;
Iatrou H, Siakali-Kioulafa E, Hadjichristidis N, Roovers J, Mays JW. "Hydrodynamic properties of model 3-miktoarm star copolymers". J Polym Sci Polym Phys Ed 1995;33:1925–32;
Pochan DJ, Gido SP, Pispas S, Mays JW. Morphological transitions in an I2S simple graft block copolymer: from folded sheets to folded lace to randomly oriented worms at equilibrium. Macromolecules 1996;29:5099–105;
Pispas S, Mays JW, Pochan D, Gido SP, Hadjichristidis N. Synthesis, characterization, and morphology of model graft copolymers with trifunctional branch points. Macromolecules 1996;29:7022–8;
Lee C, Gido SP, Poulos Y, Hadjichristidis N, Beck Tan N, Trevino SF, et al. H-shaped double graft copolymers: Effect of molecular architecture on morphology. J Chem Phys 1997;107:6460–9;
Lee C, Gido SP, Pitsikalis M, Mays JW, Beck Tan N, Trevino S, et al. Asymmetric single graft block copolymers: effect of molecular architecture on morphology. Macromolecules 1997;30:3732–8;
Lee C, Gido SP, Poulos Y, Hadjichristidis N, Beck Tan N, Trevino SF, et al. Π-Shaped double-graft copolymers: effect of molecular architecture on morphology. Polymer 1998;39:4631–8.
[18] Morton M, Helminiak TE, Gadkary SD, Bueche F. Preparation and properties of monodisperse branched polystyrene. J Polym Sci 1962;57:471–82.
[19] Iatrou H, Mays JW, Hadjichristidis N. Regular comb polystyrenes and graft polyisoprene/polystyrene copolymers with double branches ("centipedes"). Quality of (1, 3-Phenylene)bis(3-methyl-1-phenylpentylidene)dilithium Initiator in the presence of polar additives. Macromolecules 1998;31:6697–701.
[20] Uhrig D, Mays JW. Synthesis of combs, centipedes, and barbwires: poly(isoprene-graft-styrene) regular multigraft copolymers with trifunctional, tetrafunctional, and hexafunctional branch points. Macromolecules 2002;35:7182–90.
[21] Milner S. Chain architecture and asymmetry in copolymer microphases. Macromolecules 1994;27:2333–5.
[22] Beyer FL, Gido SP, Buschl C, Iatrou H, Uhrig D, Mays JW, et al. Graft copolymers with regularly spaced, tetrafunctional branch points: morphology and grain structure. Macromolecules 2000;33:2039–48.
[23] Weidisch R, Gido SP, Uhrig D, Iatrou H, Mays JW, Hadjichristidis N. Tetrafunctional multigraft copolymers as novel thermoplastic elastomers. Macromolecules 2001;34:6333–7.
[24] Staudinger U, Weidisch R, Zhu Y, Gido SP, Uhrig D, Mays JW, et al. "Mechanical properties and hysteresis behaviour of multigraft copolymers". Macromol Symp 2006;233:42–50.
[25] Sumpter BG, Mays JW, Noid DW, Gido SP, Weidisch R. Feature article: experimental design and molecular modeling of novel graft copolymers. Polym News 2004;29:302–10.
[26] Staudinger U, Schlegel R, Weidisch R, Fritzsche J, Klüppel M, Heinrich G, et al. Interpretation of hysteresis behaviour of PI–PS multigraft copolymers by adapting to the dynamic flocculation model. Eur Polym J 2008;44:3790–6.
[27] Schlegel R, Wilkin D, Duan Y, Weidisch R, Heinrich G, Uhrig D, et al. Stress softening of multigraft copolymers. Polymer 2009;50:6297–304.
[28] Schlegel R, Staudinger U, Thunga M, Weidisch R, Heinrich G, Uhrig D, et al. Investigations on mechanical properties of PI–PS multigraft copolymers. Eur Polym J 2009;45:2902–12.
[29] Duan Y, Thunga M, Schlegel R, Schneider K, Rettler E, Weidisch R, et al. Morphology and deformation mechanisms and tensile properties of tetrafunctional multigraft copolymers. Macromolecules 2009;42:4155–64.

David Uhrig graduated from the University of Alabama at Birmingham in 2001, earning a Ph.D. in Chemistry under the supervision of Jimmy Mays. He then served a postdoctoral appointment at both the University of South Australia and Flinders University with Professor Janis Matisons. From 2004, he has worked at Oak Ridge National Laboratory, where he currently remains as a technical staff.

Ralf Schlegel (born 1976) received his Master (Dipl.-Ing. In German) at Technische Universität Dresden in 2002. In 2006 he joins the Institute of materials science and technology in Jena as a Ph.D. candidate. Since 2010 he has been at the Fraunhofer Institute for Mechanics of Materials IWM. His interest is in the area of deformation behaviour of thermoplastic elastomers and block copolymers, mechanical characterization and modelling, and structure property correlations.



Prof. Dr.-Ing. habil. Roland Weidisch is currently a Professor at the Martin-Luther-Universität (MLU) Halle-Wittenberg Institut für Chemie, Germany and the Business Director of Polymer Application Fraunhofer institute of Materials of Mechanics, Germany. He had his education in Habilitation at Martin-Luther Universität Halle-Wittenberg, Fachbe-reich Ingenieurwissenschaften. He received his Ph.D at the Martin-Luther Universität Halle-Wittenberg, Institut für Werkstoffwissenschaft under the guidance of Prof. Dr. G. H. Michler. He had held many posts such as a professor of Mechanics of functional Materials at FSU Jena between 2006 and 2010, lecturer in Angewandte Mechanik" at IMT at FSU Jena between 2005 and 2006, assistant professor and team leader at IPF Dresden etc,. One of the many publication most relevant to the proposal is M. Ganß, B. K. Satapathy, M. Thunga, R. Weidisch, K. Knoll: **Molecular-Weight-Controlled Brittle-to-Semiductile-to-Ductile Transition in S-(S/B)-S Triblock Copolymers**. *Macromolecular Materials and Engineering 2010, 295, 178. Another significant publication is* 1. R. Schlegel, D. Wilkin, Y. Duan, R. Weidisch, G. Heinrich, D. Uhrig, J.W. Mays, H. Iatrou, N. Hadjichristidis: **Stress softening of multigraft copolymers**. *Polymer 2009, 50 (26), 6297. Some of his synergistic activities include being the* Organizer of the international symposium" Functional Polymer Based Materials in 2007 and a visiting researcher at University of Tennessee, Dept. of Chemistry in 2003. He can be mailed at the below email id E-Mail: roland.weidisch@chemie.uni-halle.de, roland.weidisch@iwmh.fraunhofer.de.

Jimmy Mays (born 1957) received his Ph.D. from the University of Akron in 1984 under the direction of Lewis J. Fetters. After four years in industry with Hercules Incorporated, he joined the faculty at the University of Alabama at Birmingham. In 2002 he moved to his current position as UT/ORNL Distinguished Scientist at the University of Tennessee and Oak Ridge National Laboratory. Dr. Mays is a fellow of the Polymer Chemistry Division of the American Chemical Society, and in 2009 he received the ACS Southern Chemist Award. His research is focused on synthesis of well-defined polymers and copolymers of complex architecture.